

Appl. No. : Unknown
Filed : Herewith

September 25, 1996, issued January 18, 2000 as U.S. Patent No. 6,015,590, which is the National Phase U.S. application of PCT application No. PCT/FI95/00658, claiming the priority benefit under 35 U.S.C. §119 from Finnish Application No. 945611, filed November 28, 1994.

Field of the Invention

Please replace the paragraph beginning on page 1, line 3, with the following amended paragraph:

A3
The present invention relates to a method for growing thin films on substrates in a reaction space by alternate repeated reactions of at least two vapor phase reactants with the substrates.

Please replace the paragraph beginning on page 1, line 24, with the following amended paragraph:

A4
The invention also concerns an apparatus suited for producing thin films, comprising a reaction chamber with gas flow channels suited for an inflow of vapor phase reactant pulses and an outflow of reaction products, wherein at least a portion of the gas flow channels have a narrow, oblong cross-section for minimizing the volume of the reaction space.

On page 2, line 3, please insert the following heading:

A5
Background and Summary of the Invention

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Please replace the paragraph beginning on page 2, line 6, with the following amended paragraph:

A6
0985331-05401
Con Conventionally, thin-films are grown using vacuum evaporation deposition, the Molecular Beam Epitaxy (MBE) and other vacuum deposition methods, different variants of the Chemical Vapor Deposition (CVD) method, including low-pressure and organometallic CVD and plasma-enhanced CVD, or alternatively, the above-described deposition method of alternately repeated surface reactions called the Atomic Layer Epitaxy (ALE) method. In the MBE and CVD methods, besides other process variables, the thin-film growth rate is also affected by the concentrations of the starting material inflows. To achieve a uniform thickness of the layers deposited by the first category of conventional methods, the concentrations and reactivities of starting materials must hence be carefully kept constant all over the substrate area. If the starting materials are allowed to mix with each other prior to reaching the substrate surface as is the case in the CVD method, for instance, a chance of their premature mutual reaction arises. Then, the risk of microparticle formation already within the inflow channels of the gaseous reactants is imminent. Such microparticles have a deteriorating effect on the quality of the thin film growth. Therefore, the possibility of premature reactions in MBE and CVD reactors is avoided by heating the starting materials no earlier than at the substrate surfaces. In addition to heating, the desired reaction can be initiated using, e.g., a plasma or other similar activating means.

Please replace the paragraph beginning on page 2, line 24 with the following amended paragraph:

A7
In the MBE and CVD processes, the growth of thin films is primarily adjusted by controlling the inflow rates of starting materials impinging on the substrate. By contrast, the ALE process is based on allowing the substrate surface qualities, rather than the starting material concentrations or flow variables, to control the deposition rate. The only prerequisite in the ALE process is that the starting material is available in sufficient concentration for thin-film formation on all sides of the substrate.

Please replace the paragraph beginning on page 3, line 8 with the following amended paragraph:

A8
0985331-051401
In the ALE growth method, atoms or molecules are arranged to sweep over the substrates, thus continuously impinging on their surface so that a fully saturated molecular layer is formed thereon. According to the conventional techniques known from the FI patent publication No. 57,975, the saturation step is followed by an inert gas pulse forming a diffusion barrier which sweeps away the excess starting material and the gaseous reaction products from above the substrate. The successive pulses of different starting materials and of diffusion barriers of an inert gas separating the former accomplish the growth of the thin film at a rate controlled by the surface chemistry properties of the different materials. Such a reactor is called the "traveling-wave" reactor. To the function of the process it is irrelevant whether the gases or the substrates are moved, but rather, it is imperative that the different starting materials of the successive reaction steps are separated from each other and arranged to impinge on the substrate successively.

Please replace the paragraph beginning on page 4, line 1 with the following amended paragraph:

A9
In conventional ALE apparatuses, a characterizing property is that the different starting materials of the reaction are understood to be isolated from each other by means of a diffusion wall formed by an inert gas zone traveling between two successive pulses of starting materials, cf. above-cited FI patent publication No. 57,975 and the corresponding US Pat. No. 4,389,973. The length of the inert gas zone acting as the downstream flowing diffusion wall is such that only

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approx. one millionth of the reactant gas molecules have a sufficient diffusion velocity to travel under the prevailing conditions in the counterflow direction to a distance greater than the thickness of the isolating diffusion wall employed in the method--.

Please replace the paragraph beginning on page 4, line 30 with the following replacement paragraph:

0985331-051401
P410
--The goal of the invention is achieved by virtue of admitting vapor-phase pulses of the starting material reactants into the ALE reactor so that each starting material pulse is individually driven through the piping and reaction space of the apparatus isolated from the other pulses. According to the invention, this concept is implemented by means of purging the gas volume of the reaction space between two successive vapor-phase pulses essentially entirely, which means a purging efficiency of at least 99 %, advantageously 99.99 %. Thence, all the reacting gas, which in practice refers to the entire gas volume filled with the vapor-phase reactant, is purged from the reaction space between the successive pulses. Thus, the reactant pulses of different starting materials remain isolated from each other, whereby no mixing of the reactants can occur.--.

Please replace the paragraph beginning on page 5, line 20 with the following amended paragraph:

A11
--More specifically, the method according to the invention is principally characterized by a reaction space in which the gas volume is evacuated essentially totally between two successive vapor phase reactant pulses.--.

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Please replace the paragraph beginning on page 5, line 23 with the following amended paragraph:

A12
Furthermore, the apparatus according to the invention is principally characterized by a reaction chamber with gas flow channels suited for an inflow of vapor phase reactant pulses and an outflow of reaction products, wherein at least a portion of the gas flow channels have a narrow, oblong cross-section for minimizing the volume of the reaction space.--

Please replace the paragraph beginning on page 6, line 4 with the following replacement paragraph:

095534-05443
A13
In the present context, the term "inactive" gas is used to refer to a gas which is admitted into the reaction space and is capable of preventing undesired reactions related to the reactants and the substrate, respectively. Such reactions include the reactions of the reactants and the substrate with possible impurities, for instance. The inactive gas also serves for preventing reactions between the substances of the different reactant groups in, e.g., the inflow piping. In the method according to the invention, the inactive gas is also used advantageously as the carrier gas of the vapor-phase pulses of the reactants. According to a preferred embodiment, in which the reactants of the different reactant groups are admitted via separate inlet manifolds into the reaction space, the vapor-phase reactant pulse is admitted from one inflow channel while the inactive gas is admitted from another inflow channel, thus preventing admitted reactant from entering the inflow channel of another reactant. Of inactive gases suited for use in the method, reference can be made to inert gases such as nitrogen gas and noble gases, e.g., argon. The inactive gas may also be an inherently reactive gas such as hydrogen gas serving to prevent undesirable reactions, e.g., oxidization reactions, from occurring on the substrate surface.--

Please replace the paragraph beginning on page 6, line 21 with the following amended paragraph:

A14
0985331.064401
1047507.235860
According to the invention, the term "reaction space" includes both the space in which the substrate is located and in which the vapor-phase reactants are allowed to react with the substrate in order to grow thin films, namely, the reaction chamber, as well as the gas inflow/outflow channels communicating immediately with the reaction chamber, said channels serving for admitting the reactants into the reaction chamber, inflow channels, or removing the gaseous reaction products of the thin-film growth process and excess reactants from the reaction chamber, outflow channels. According to the construction of the embodiment, the number of the inflow and outflow channels, respectively, can be varied from one upward. According to the invention, the reaction space is the entire volume to be evacuated between two successive vapor-phase pulses.

Please replace the paragraph beginning on page 7, line 28 with the following amended paragraph:

A15
A characterizing property of the present invention is that the different starting materials are not allowed to flow simultaneously in the piping or reactor, reaction space, but rather, the piping and reaction space are evacuated from the contents of the preceding vapor-phase pulse prior to the admission of the next vapor-phase pulse. Advantageously, the interval between the successive pulses is kept so long as to permit the evacuation of the reaction space using at least a double or triple purging gas volume during the interval between the pulses. To achieve maximally efficient evacuation of reactant residues, the reaction space is purged with an inactive gas during the interval between the reactant pulses and the total volume of gas evacuated from the reaction space during the interval between the reactant pulses amounts to at least 2 - 10 times the volume of the reaction space. A design target value of less than 1 %, advantageously less than 1 %, of residual components of the preceding vapor-phase reactant pulse remaining at the infed of the next pulse can be set for the evacuation efficiency. Operation according to the

Please replace the paragraph beginning on page ~~10~~, line ~~20~~ with the following amended paragraph:

- Typically, the flat gas flow channel according to the invention has a cross section with a width, orthogonal to the flow direction of the gas pulse front, of approx. 1 - 100 times the channel height. Advantageously, the width-to-height ratio is approx. 5:1 - 50:1, typically approx. 30:1 - 5:1.

Please replace the paragraph beginning on page 11, line 13 with the following amended paragraph:

According to a particularly advantageous embodiment, the apparatus according to the invention comprises vertically or horizontally stacked planar elements, whereby said elements have recesses/grooves corresponding to the reaction chambers and gas flow channels machined to them and at least a number of said elements is mutually identical. The edge areas of the planar elements are provided with round, or alternatively, oblong notches or openings extending through the planar element and forming said gas flow channels of said reaction space when said planar elements are stacked vertically or horizontally in order to form a reaction chamber pack. The number of the round openings on the reactant inflow side is advantageously one per each reactant group, which in practice means two openings. The number of oblong openings required on the outflow side is only one.

On page 13, line 11, please insert the following heading:

--Brief Description of the Drawings--

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On page 13, line 19, please insert the following heading:

~~Detailed Description of the Preferred Embodiments~~

Please replace the paragraph beginning on page 14, line 10 with the following amended paragraph:

~~When stacking the planar elements, between each two superimposed elements is placed an intermediate plate 6 suited for controlling the constriction of the gas flow by setting the cross section of the inlet slit 8 from the inflow channel 7 into the reaction chamber 13 and the cross section of the outlet slit 14 from the reaction chamber to the outflow channel 4.~~

Please replace the paragraph beginning on page 14, line 16 with the following amended paragraph:

~~The upper half of the uppermost reaction chamber acts as the top plate 9 of the reaction chamber pack, and correspondingly, the lower half of the lowermost reaction chamber acts as the bottom plate 11, which is mounted onto a support base 17. Between said top plate and bottom plate are stacked three mutually identical planar elements 10. Each planar element forms firstly in combination with the substrate 12 the wall between two adjacently stacked reaction chambers, and secondly, in combination with the intermediate plates 6 and other auxiliary plates, forms the inflow and outflow channels 7, 4. The number of the planar elements may be varied in the range 0 - 100 pcs.~~

Please replace the paragraph beginning on page 15, line 27 with the following amended paragraph:

~~Ensuring the equalized cross-directional outflow pattern of gas front is extremely important, because the gas molecules tend to travel toward the direction of lowest pressure, most effective suction, whereby the straight gas front will be distorted if subjected to a~~

nonhomogeneous suction. Moreover, a homogeneous suction effect will rectify a gas front distorted due to other possible reasons.

Please replace line 17 on page 18 with the following amended line:

A23 --Total volume of reaction chambers $5 \times 300 \times 300 \times 4 \text{ mm}^3 = 1,800 \text{ cm}^3$ --

Please replace line 25 on page 18 with the following amended line:

A24 --Total volume $2,400 \text{ cm}^3$, or approx. 2.4 L--

Please replace the paragraph beginning on page 18, line 27 with the following amended paragraph:

A25 --The pump capacity is selected as $360 \text{ m}^3/\text{h}$, or $360 \times 1000/3600 \text{ (l/s)} = 100 \text{ l/s}$. Hence, the above-calculated total gas volume can be evacuated with a pump so dimensioned in approx. 0.024 s.--

Please replace line 1, page 20 with the following amended line:

--WE CLAIM:--.